Batteries
fifty years of materials development

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Abstract

This paper reviews developments in batteries over the past 50 years with particular reference to advances in materials science and engineering technology. The emphasis is on commercially available batteries such as zinc/manganese dioxide primary cells, and lead/acid and nickel/alkaline secondary cells, although specialist batteries and those in an advanced stage of development are also described briefly. Rechargeable lithium-ion batteries will be covered in another paper in this symposium. © 2000 Ronald M. Dell. Published by Elsevier Science B.V.

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1. Introduction

Fifty years is a long time in the history of materials science, and also in the design, development and application of primary and secondary batteries. In the 1940s, the principal domestic uses for batteries were in torches (flashlamps), in a few toys, in vehicles (for starting, lighting and ignition) and in radios. Before the days of transistors and solid state electronics, when thermionic valves (tubes) were used in radios, it was necessary to have a source of low voltage electricity to heat the filament and a DC high voltage to accelerate electrons between the valve cathode and anode. Many radios in those days were remote from the electricity supply and then two batteries were required, a 2 V lead/acid accumulator to supply the filament current and a 'high tension' battery consisting of 100 or 120

Leclanché cells wired in series to supply the high DC voltage. The radio weighed several kilograms, had to be maintained in an upright position to avoid spillage of acid and was anything but 'portable'. No doubt there were other applications for batteries in industry and commerce, for example emergency lighting and back-up for the primitive telephone system of the day.

Over the past 50 years the applications for small batteries in the home (consumer batteries) have expanded phenomenally. Today small primary or rechargeable batteries are employed in a huge number of appliances. Some examples are as follows.

- Household: telephones, clock-radios, security alarms, smoke detectors, portable fluorescent lamps, torches and lanterns, car central locking activators, door-chimes.
- Workshop and garden: portable tools (e.g. screwdrivers, drills, sanders), portable test meters, hedge trimmers, lawnmowers.

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- Entertainment: portable radios and TVs, compact disc players, tape recorders, keyboards, electronic games and powered toys.
- Personal hygiene and health: toothbrushes, bathroom scales, hair trimmers, shavers, blood pressure monitors, hearing aids, heart pacemakers.
- Portable electronic devices: watches, cameras, camcorders, calculators, organisers, mobile phones, laptop and notebook computers, bar code readers.

With all these new applications, which have developed over the past few decades, the market for consumer batteries has grown correspondingly. Today the average family may have as many as 40–60 consumer batteries at any one time in and around the home. Many of these will be batteries of advanced design and construction, giving greatly improved performance as a result of developments in materials science and technology. Although most small consumer batteries are still of the primary (throw-away) variety, there is a growing trend to adopt secondary (rechargeable) batteries as being more economical.

There has been a similar mushrooming in demand for large size, installed battery packs. Almost every public building (hotels, supermarkets, multiple stores, railway stations, airports, hospitals etc.) must have an uninterruptable power supply and this requires a battery pack to take over seamlessly when the mains supply fails, until such time as a local generator can be started. Most factories, office blocks, ships, aircraft, telephone exchanges and even power stations have their own uninterruptable supply. Other applications for large primary or rechargeable batteries are in the defence field (submarine traction batteries, torpedoes, missiles), in space vehicles (satellites, space probes), in solar energy storage (remote area power supplies, navigation beacons) and in electric and hybrid vehicles (tugs and tractors, forklift trucks, invalid conveyances, golf carts, milk floats and other road vehicles). Although many of these applications utilise long-established lead/acid or nickel/cadmium rechargeable batteries, these have been transformed over recent decades by advances in materials and design. Moreover, there are now specialised batteries with unconventional chemistries, particularly for use in

the military and space fields, and in the past decade new rechargeable batteries have been introduced into civilian and consumer markets.

This article is intended as an introductory overview of improved batteries and of the advances in materials science and development which have led to them. The emphasis is on commercially available batteries, such as zinc/manganese dioxide primary batteries and lead/acid secondary batteries. These long-established electrochemical couples still command major market shares. However, materials science advances have resulted in new battery types, such as nickel/metal hydride, and these are described in outline. Lithium rechargeable batteries are not covered in any detail as they are the subject of another paper at this symposium.

2. Consumer batteries

2.1. Zinc/manganese dioxide (1.5 V) primary cells

Fifty years ago most primary batteries were of the Leclanché type in which the zinc negative electrode was in the form of a metal can which acted as the container for the other cell components. There was a central carbon rod which served as the positive electrode and this was surrounded by a mixture of crude MnO_2 (often the mineral pyrolusite) and carbon powder, intimately mixed together. The function of the carbon powder was to increase the conductivity of the positive active mass and so to reduce the internal resistance of the cell. The electrolyte, an aqueous solution of ammonium chloride and zinc chloride, was absorbed into the pores of a paste type separator (e.g. starch) and the MnO_2/C mixture, and for this reason these cells became known as 'dry cells'. The cells had a seal and vent at their upper end and a non-conducting board cap which served to insulate the positive carbon rod from the negative zinc can. Finally, the zinc can was surrounded by a cardboard jacket, on which the manufacturer's name and information was printed.

Over the years some improvements have been made in the design of Leclanché cells and their materials of construction. The metallurgy of the zinc can has been improved through alloying additions to facilitate deep drawing. Better designs of seals have

been developed. The use of mercury to increase the over-potential for hydrogen evolution at the zinc electrode has been largely phased out for environmental reasons. The cardboard jacket is now replaced by a steel container coated with polymer and a polyester film label. This steel outer case is insulated from the zinc can. The insulating cell cap is made of a hard polymer rather than board. These improvements greatly reduce the tendency of the cells to leak electrolyte when fully discharged, which used to be a serious problem.

Leclanché cells are in declining use today. Although cheap to manufacture and purchase, they suffer from a number of limitations:

- they are not suitable for high-drain applications (such as driving electric motors) as they readily polarise and the available capacity falls sharply with increased discharge rate;
- their shelf life is not especially long;
- the optimum temperature range of operation is 20–40°C; outside of this temperature range the performance deteriorates markedly.

Leclanché cells are best suited to low drain intermittent use, with rest periods for recuperation (depolarisation) to take place, and for use within 1–2 years. A good example is a domestic flashlamp battery. They may also be used in low-drain applications such as door-chimes or smoke detectors, but then their relatively short operational life becomes a nuisance as they require periodic replacement.

Superficially, the electrochemistry of the Leclanché cell is simple. At the negative electrode zinc metal is oxidised to Zn^{2+} ions

$$Zn \Rightarrow Zn^{2+} + 2e$$
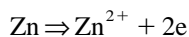
while at the positive electrode manganese dioxide is reduced to trivalent manganese with resultant rise in pH

$$2MnO_2 + 2H_2O + 2e \Rightarrow 2MnO.OH + 2OH^-.$$
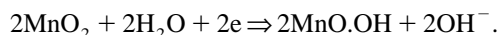
In reality, the cell reactions are much more complex than this, with the intermediate formation of sparingly soluble species such as $Zn(NH_3)_2Cl_2$ and $ZnCl_2.4Zn(OH)_2$, particularly at high discharge rates, and these solids tend to impede ionic diffusion

necessary for cell discharge. The resulting fall in pH near the zinc anode leads to enhanced chemical corrosion, with liberation of hydrogen. As the internal pressure in the cell rises, the seals ultimately leak, forcing electrolyte to the exterior of the cell.

Many of these problems are overcome in the *zinc chloride* cell which has a simpler chemistry as the ammonium chloride electrolyte is replaced entirely by $ZnCl_2$ solution. The reduced tendency for the electrodes to be blocked by product solids permits faster diffusion and higher rate discharge. A better quality grade of MnO_2, prepared electrolytically, is employed and a greater proportion of carbon black to facilitate the cathodic reaction. The cells also have a more sophisticated seal design and these factors, taken together, result in a higher cost of manufacture to offset the improved performance. Zinc chloride cells fall between Leclanché and alkaline manganese cells as regards both performance and cost. They perform better than Leclanché for high drain applications and, particularly, for use at low temperature (to −20°). These two types of cell together are known generically as *zinc/carbon cells*.

Alkaline manganese, the premium form of Zn/ MnO_2 cell, differs from zinc/carbon in a number of important respects. A principal difference lies in the use of a different electrolyte, viz. concentrated (~30%) potassium hydroxide solution. Another significant difference is in the nature of the zinc electrode which consists of finely divided zinc powder packed around a brass current collector at the centre of the cell. A third difference lies in the cell configuration; the cathode mix, of electrolytic MnO_2 and fine graphite powder, is packed around the *outside* of the zinc anode and separator and is in electrical contact with the nickel-plated steel can (Fig. 1). This inversion of the cell configuration might be expected to lead to an inversion of polarity of the terminals. As this would be unacceptably confusing to the consumer, the problem is overcome by bringing the central current collector (negative) into contact with the cell base, rather than the cap, and having the insulating seal at the *bottom* of the cell rather than the top, with the steel can contacting the top (positive) terminal.

Because concentrated potassium hydroxide electrolyte is chemically reactive, and is also prone to flow (creep) along surfaces, the development of
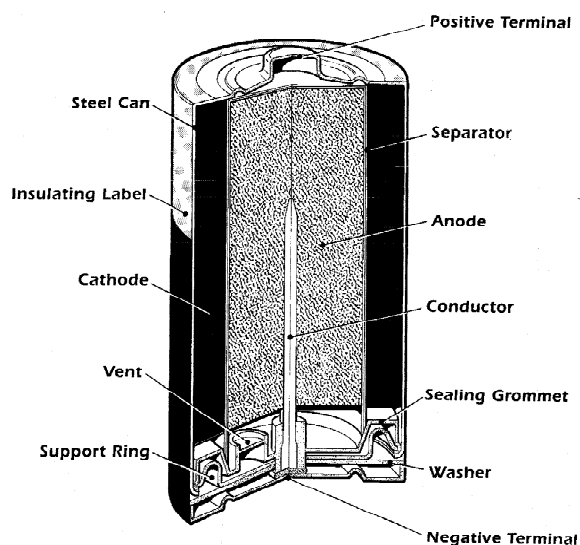
Fig. 1. Construction of an alkaline manganese primary cell.

satisfactory seals for the alkaline manganese cell was a technical challenge which had to be solved before the cells could be commercialised. Modern cells have effective seals which are resistant to leakage and corrosion.

Alkaline manganese cells, which retail at a premium price, are more suitable than zinc/carbon cells for continuous high drain applications and for use at low temperatures. They also have a longer shelf life of >4 years at 20°, making them attractive for low drain 'fit and forget' applications such as smoke detectors. However, their principal economic advantage is seen in high drain applications such as children's toys, cassette players, electric shavers, etc.

where the effective capacity delivered is many times that of a Leclanché cell under similar conditions. Table 1 makes a comparison of the approximate service life of alkaline manganese and zinc/carbon cells at various discharge rates. It will be seen that the ratio of hours service (alkaline manganese/Leclanché) is greater for the large D size cells than for the smaller AA cells and also greater at high discharge rates (small loads). At very low discharge rates the ratio falls to about 2 at 21°C, but rises again sharply at temperatures below 0°C. It will be clear that major advances have been made in the design and construction of Zn/MnO_2 cells over the past 40 years, with new materials playing a significant role in this success.

Recently at least two companies have introduced a premium grade of alkaline battery for high drain applications. Materials science advances have been responsible for these developments through reducing the internal resistance of the cells. In one case this is said to be as a result of coatings deposited on the anode and cathode current collectors; in the other the result of using a finer grade of graphite powder and packing more MnO_2 powder into the available cathode space. The claims for the improvements in discharge power and service life are quite impressive.

Zn/MnO_2 cells are made in a number of sizes and configurations. The most popular sizes are AAA, AA, C and D, although both smaller and larger cells are available. Another popular item is the prismatic 9 V (PP3) battery. This consists of six small cells lying flat (i.e. perpendicular to the long axis of the case) and joined in series. These 9 V batteries are ideal for low drain applications such as smoke detectors.

Table 1

Comparison of approximate service lives of alkaline manganese and zinc/carbon cells at different discharge rates[a]

Cell size	AA			Load (ohms)	D		
Cell type Load (ohms)	Zn/C Hours	Alk.Man. Hours	Ratio		Zn/C Hours	Alk.Man Hours	Ratio
62	35	140	4	10	13	130	10
24	12	50	4	4.7	6	50	8
3.9	0.9	9	10	2.2	1.5	20	13

[a] Data published by Duracell for discharge to 0.8 V at 21°C.

2.2. Zinc/manganese dioxide secondary cells

Traditionally, the Zn/MnO_2 cell has always been seen as a primary (throw-away) unit. In the past few years developments in materials, and also in electronic charge/discharge control, have led to the *Rechargeable Alkaline Manganese (RAM) cell*. The incentive for recharging alkaline manganese cells is considerable as shown by the following comparative figures for the capacity of an AA sized cell:

Alkaline manganese 2–3 Ah
Nickel/cadmium 0.5–1.0 Ah
Nickel/metal hydride 1–1.5 Ah

When recharged after 100% depth of discharge (DOD), RAM cells are capable of providing at least 10 times the service hours of single use alkaline cells, while if discharge is restricted to about 20% many more hours of service may be obtained. Under conditions of low DOD cycling, up to 200 Ah cumulative charge is possible from a 2.5 Ah RAM cell. Bearing in mind that these cells are cheaper than Ni/Cd, and do not suffer from the memory effect or from recycling problems with toxic cadmium, the attraction of RAM cells is obvious, even though their cycle life is less than Ni/Cd.

What are the advances which have made possible the recharging of alkaline manganese cells? Firstly, new separators were developed which are highly stable in the strongly alkaline environment and which prevent zinc dendrite formation (leading to internal short circuiting). Measures were also taken to prevent swelling of the cathode. The manganese oxide electrode was made rechargeable by limiting the capacity of the zinc electrode so that discharge does not take place beyond the first electron $(Mn^{4+} \rightarrow Mn^{3+})$, corresponding to a cut-off voltage of 0.9 V/cell. To allow for hydrogen formed by corrosion, catalysts are added to the cathode mix so as to facilitate the recombination of H_2 gas and also to provide overcharge protection via the oxygen recombination cycle. Special chargers have been designed to taper charge RAM cells to a maximum of 1.7 V/cell, so as to prevent overcharge and gassing.

Industry has been slow to introduce RAM cells for fear of upsetting the primary battery market, but they are now available in the shops, along with the custom designed chargers, and it seems likely that this will be a rapidly growing market in the near future for those who are prepared to take the trouble of recharging their cells. Correspondingly, it seems likely that rechargeable Ni/Cd consumer cells will decline in popularity.

2.3. Button cells and miniature batteries

A major advance of the past 30 years has been the development of button and coin cells, and miniature batteries, for use in clocks, watches, hearing aids, car alarms, key locks etc. These may be based on any one of several different chemistries. The first button cell to be introduced in the 1940s was the *zinc/ mercury oxide cell*. Later, in the 1960s, the *zinc/ silver oxide cell* was developed to meet the new market of electric watches (Fig. 2). Both cells employ alkaline electrolytes. Attractive features of these batteries are their high volumetric energy density of 500–550 mWh/cm^3 (cf. alkaline MnO_2 350 mWh/cm^3) and their particularly flat discharge curves, even under continuous drain at low currents (μA–mA). The anode in both cell types is an amalgamated pellet of zinc powder and the cathode a pellet of HgO or Ag_2O_2 mixed with carbon. Provision has to be made in the cell design for the venting of hydrogen, which may arise through corrosion, and there is a safety sleeve filled with absorbent material to take up any displaced electrolyte. These zinc-based button cells are particularly suited to applications requiring constant discharge voltage, but they are gradually being replaced by lithium cells on environmental and cost grounds.

Another option for the alkaline zinc cell is to employ an air cathode, with technology similar to that in the alkaline fuel cell. The primary *zinc/air cell* is half battery, half fuel cell and has been developed in button form particularly for the hearing-aid market where the attraction lies in the high volumetric energy density of the cell (~650 mWh/ cm^3). The development of a satisfactory air cathode provided the greatest technical challenge. For the electrode reaction to take place, it is necessary to ensure three-phase contact between the air, the KOH electrolyte and the solid electrode and also to employ a good catalyst for oxygen reduction. This was
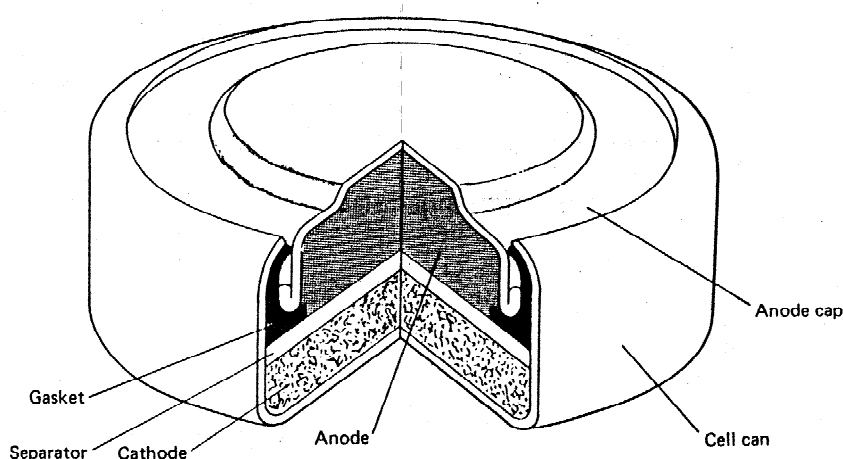
Fig. 2. Cutaway view of zinc–silver oxide button cell.

achieved by using a porous nickel or carbon matrix, coated with catalyst, and with a water repellant outer surface so as to maintain a stable liquid meniscus within the thin cathode and also to minimise loss of water by evaporation. To prevent absorption of CO_2 by the electrolyte during the shelf life of the cell, the air inlet is sealed and the seal has to be broken before bringing the cell into use.

3. Lithium batteries

For 15–20 years there has been enormous international activity in the development of lithium batteries, both primary and secondary. The interest stems from the low atomic mass of lithium (6.94), its high specific capacity (3.86 Ah/g) and its high electrochemical reduction potential (−3.045 V), all of which contribute to a high specific energy for lithium cells.

Primary cells normally employ lithium metal foil as anodes, whereas secondary lithium cells are not usually based on lithium metal since experience has shown that repeated recharging of lithium metal anodes can be dangerous. Rather, most rechargeable lithium cells are of the 'lithium ion' type in which Li^+ ions are intercalated into a carbon anode in the charged state and into an oxide cathode in the discharged state.

Numerous cathode compounds have been used in lithium primary cells, e.g. CuO, CuS, CF_x, MnO_2,

MoO_3, V_2O_5 etc. Commercially, the most widely adopted positive-electrode materials are CF_x, and MnO_2. The electrolyte employed in lithium cells is a solution of a lithium salt in an organic solvent. The number of possible combinations of salt and solvent is large, and most lithium cell manufacturers have their own preferred solution.

Lithium/manganese dioxide primary cells are manufactured in a standard range of cell sizes for consumer applications, as well as button cells and special thin cells sized to customers' requirements. These cells are noted for their high specific energy (260 Wh/kg), flat discharge curves, wide operating temperature range (−40 to +60°C), and long shelf life (up to 10 years). It is the latter factor which is causing them to replace alkaline primary cells in smoke detectors in the USA. The standard bobbin cells are only suited to low rate applications, but there is also available a cell constructed on the 'jelly roll' principle (Fig. 3) which may be discharged at the 2–4 h rate. This is finding widespread use in portable radio communications.

There are several other types of lithium primary cell which find specialised application.

1. Lithium/iodine cells: these are all-solid-state cells comprising a lithium foil anode and a positive made from a chemical complex of iodine and poly-2-vinyl pyridine. When these two solids are brought into contact a thin film of lithium iodide is formed and this serves as a solid electrolyte.
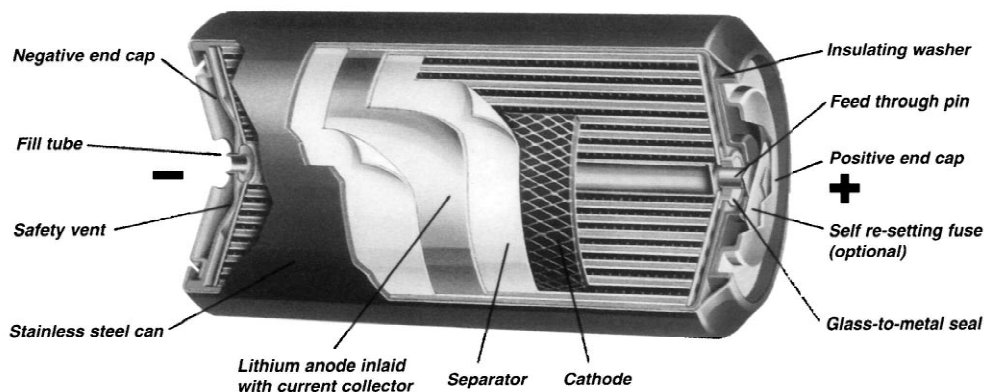
Anatomy of a Cell

Fig. 3. Construction of a high rate lithium/manganese dioxide cell.

Although this electrolyte has a low ionic conductivity, the film is very thin and the conductance is adequate for low drain (μA) service. These solid-state cells have no electrolyte to leak and are ideal for use where this could be a major concern. They are widely employed in heart pacemakers and, to some extent, in watches and pocket calculators.

2. Lithium/thionyl chloride cells: these are large, high rate primary cells which are used in military applications such as naval sonar buoys and space power. The discharge reaction is

$$4Li + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S \qquad V^0 = 3.6 \text{ V}$$
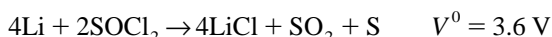
The cell has a high specific energy (330 Wh/kg), a high energy density (>700 Wh/dm^3), a good low temperature performance and a long shelf-life.

3. Lithium/iron sulphide cells: these cells are used as power sources in missiles and rockets where the discharge time is short (~minutes). They have a molten salt electrolyte (a eutectic of lithium halides) and operate at high temperatures (typically 400–450°C). A great deal of materials research has gone into developing this concept. The anode is a Li/Al alloy and the cathode FeS$_2$. The cell is heated to operating temperature by a pyrotechnic charge. The characteristics of these cells, which match to the application, is that they are able to provide enormous power output for short intervals

and have an indefinite shelf life prior to activation.

4. Lithium polymer cells: in the 1970s it was shown that certain polymers, such as polyethylene oxide, could dissolve lithium salts, giving an electrolyte with a reasonable ionic conductivity at moderate temperatures (~100°C). This research gave rise to the concept of the polymer battery. Later work has employed different polymer matrices and dissolved various organic solvents in them, along with the lithium salts, to produce electrolytes with an acceptable conductivity at room temperature and below. From this extensive materials research, carried out in many countries over a 20-year period, has evolved the lithium/polymer battery which is now becoming commercially available in rechargeable as well as primary form. Individual cells are of thickness ca. 0.5 mm and are prepared as large sheets of laminate which may be contoured into cells of any desired size or shape. The manufacture of such cells has involved the development of much new battery production technology, based largely upon that used in the paper, coatings and laminates industries.

4. Lead/acid batteries

The lead/acid battery was invented in 1859 by Planté and developed further by Faure in 1881. In the original Planté cell the active materials of the
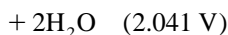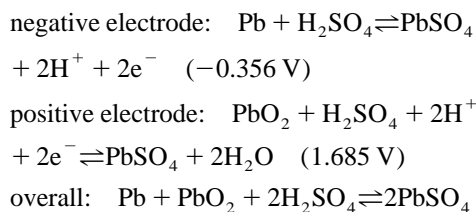
electrodes were obtained by passing a current between soft lead plates. This led to the conversion of the surface of the positive plate to PbO_2 and that of the negative plate to spongy metallic lead. Modified Planté cells are still used in many standby batteries. The innovation introduced by Faure was the pasted plate wherein a sheet of lead is coated with a paste of lead oxide and sulphuric acid. By passing a current through the cell ('forming the plates') the positive is converted to PbO_2 and the negative to spongy lead. Because of the greater mass of active material, the Faure cell has greater capacity than the Planté cell. Although invented more than 100 years ago, the lead/acid battery still has the overwhelming share of the secondary battery market.

During this century the battery has been subject to continuous improvement in materials of construction, design and manufacture, and this process is still ongoing. Many of these improvements have been of an engineering rather than scientific nature. Some examples are:

- the replacement of early glass containers by hard rubber and later by high impact polypropylene;
- the development of through-the-wall cell interconnects, rather than external cell connectors;
- heat-sealed plastic case-to-cover assemblies;
- automatic central watering systems for traction batteries;
- the development of sealed cells with safety vents.

Other improvements such as low or zero maintenance batteries, new alloys and better designs for the plates, and better separator materials have all involved a substantial scientific input. The result of this programme of work is that lead/acid batteries have shown a continuous improvement in performance and life at relatively lower costs.

The lead/acid battery is unusual in that the electrolyte, sulphuric acid, takes part in the cell charge/discharge reactions as shown:

negative electrode: $\quad Pb + H_2SO_4 \rightleftharpoons PbSO_4$

$+ 2H^+ + 2e^- \quad (-0.356\ V)$

positive electrode: $\quad PbO_2 + H_2SO_4 + 2H^+$

$+ 2e^- \rightleftharpoons PbSO_4 + 2H_2O \quad (1.685\ V)$

overall: $\quad Pb + PbO_2 + 2H_2SO_4 \rightleftharpoons 2PbSO_4$

$+ 2H_2O \quad (2.041\ V)$

The sulphuric acid is consumed during discharge and liberated during charge, allowing the state of charge to be determined by measuring the specific gravity.

The theoretical specific energy of the lead/acid battery, counting reactants only, is 170 Wh/kg, whereas in practice most real batteries deliver just 30–50 Wh/kg. This discrepancy is in part accounted for by the mass of the inactive components (cell case, grids, current collector bars, separators, terminals, etc.) and in part by poor utilisation of the active materials. The latter stems from slow diffusion processes in the porous reactants and also from the low conductivity of the discharge product ($PbSO_4$) which coats individual particles and tends to isolate them electrically.

4.1. Positive plate alloys

Conventional grid alloys are based on lead/antimony alloys containing up to 8% Sb. The role of the Sb is to strengthen and harden the Pb through the formation of a finely dispersed eutectic phase at the grain boundaries. The tensile strength, yield strength and creep resistance of the alloy all increase with Sb content. In addition, the alloying agent improves castability and the adherence of the paste to the plate. Unfortunately, the addition of antimony has attendant disadvantages also. During battery charge, the Sb dissolves (corrodes) progressively from the positive grid, diffuses through the electrolyte and deposits on the negative electrode where it reduces the over-potential for hydrogen evolution. This results in greater gassing rates, loss of water and the need for more frequent maintenance, as well as enhanced self-discharge.

In order to overcome this problem, a range of low-Sb alloys has been developed. Early attempts to use low-Sb alloys led to cracking on casting, but this was overcome by the addition of grain refining agents such as As, Cu, Se, S and Te. These enhance the stiffness, the tensile strength and the corrosion resistance of the grid alloys. Castability is improved by the addition of 0.1 wt.% Sn which increases the fluidity of lead alloys. Low-Sb alloys, as used in 'low-maintenance' automotive batteries, contain ~2 wt.% Sb.

Many automotive batteries today are of the so-called 'maintenance-free' variety in which the grids are constructed of Pb–Ca alloy (up to 0.1 wt.% Ca), sometimes with the addition of Sn or Sr. On quenching the grids during manufacture, a dispersion of Pb_3Ca forms around the pure lead grains resulting in precipitation hardening. These alloys exhibit a higher hydrogen over-potential than antimonal types and water loss during charging is largely eliminated, provided that the top-of-charge voltage is controlled. Also they have improved electrical conductivity, but are substantially weaker than their Pb/Sb counterparts. Batteries with lead/calcium grids are normally used in 'float' conditions (e.g. automotive or stand-by applications). They are unsuited to regular deep discharge as the cycle life under these conditions is strictly limited. Explanations advanced for this are complex, involving the build-up and cracking of corrosion layers on the Pb/Ca plate and structural changes in the porous active material.

4.2. Plate design and manufacture

The Planté version of the positive plate, as used in large stand-by batteries, is made from a casting of pure lead. It has a surface of vertical grooves to hold the active material, which is formed by electrochemical oxidation of the lead itself. There are two further designs of positive plate:

- grids, as used in automotive and leisure batteries;
- tubular plates, as used in traction batteries.

Traditionally, grids are cast from molten alloy, either singly or in pairs joined by their lugs, and are quench-cooled. The active material is pasted into the rectangular holes in the grid (Fig. 4). In recent years advanced techniques have been developed for the continuous casting of low-Sb grids, thereby increasing throughput and productivity. Calcium-containing grids may be made by direct casting, although a newer process is to cast a continuous strip of alloy on a water-cooled drum and subsequently to make the grid by slitting and expanding into a diamond-shaped mesh. The cast strip may be rolled (wrought) before slitting and expanding. Much research has gone into optimising the design of grids so as to maximise their conductivity and their strength for minimum mass and cost. Computer-aided design has been extensively employed.

Tubular plates consist of a row of parallel, vertical tubes, made of braided glass-fibre or woven polyester-fibre in the form of a gauntlet. Into each tube, along the central axis, is placed a thin lead alloy rod (or 'spine') which acts as current collector. These spines are cast as a single set with a common 'header' (Fig. 4) and the active material is packed into the tubes around the spines. The principal advantage of this design is that the gauntlet tube holds the active material in place, which is necessary for repeated deep discharge. The disadvantages are that the specific power of the battery tends to be lower than with grids and the manufacturing cost higher.

From this brief review it will be clear that fundamental metallurgical research has played a
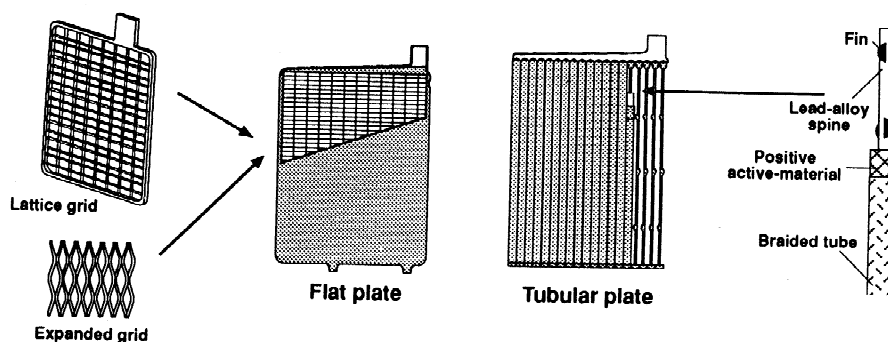

Fig. 4. Lead/acid battery plates with (a) flat plates and (b) tubular plates.

major role in lead/acid battery development in recent years, both in terms of improving the performance of batteries and in facilitating their manufacture.

4.3. Separators

Separators are interleaved between the plates of batteries so as to prevent the plates touching and giving rise to internal short circuits and also to help retain the active material in firm contact with the grids. Originally 'leaf' separators were made of natural materials such as wood veneers and paper. A more recent trend has been towards 'envelope' separators which enclose the electrode and so prevent dendritic growth around the edge which tends to occur with a leaf separator. Modern separators are generally made from a microporous polymer, such as polyethylene or polyvinyl chloride, loaded with an inorganic filler, or from glass-microfibre. These are highly sophisticated materials, into which a great deal of development work has gone. The requirements for a satisfactory separator are:

- that it should have a uniform, microporous structure (~60% porosity, pore size <1 µm);
- adequate strength and flexibility during storage and use;
- good chemical stability in battery strength sulphuric acid;
- high oxidation resistance to maximum operating temperature;
- low electrical resistance;
- high purity.

Most polymeric separators utilise a purified, precipitated silica as the carrier for a pore-forming agent such as starch or oil. The precipitated silica has a skeletal structure and is highly absorptive and acid-resistant. It is also hydrophilic and easily wetted, contributing to a low electrical resistance. The internal resistance of lead/acid batteries is measured in milliohms. The separator materials are designed with vertical ribs which provide added strength and also facilitate the convective flow of acid over the plates as its specific gravity changes during charge/discharge.

Glass-microfibre separators are used particularly in valve regulated lead/acid batteries (see Section 4.4, below). These separators are made from high purity borosilicate glass microfibres processed into sheet form by a wet process on a conventional paper-making machine. Individual fibres are of diameter 0.25–4 µm and length of ~1 mm and mostly lie in the plane of the paper. Glass-microfibre separators meet all of the above requirements for a separator and also have high compressibility, so that they conform to irregularities in the plate surface with consequent good acid transfer and low internal resistance.

4.4. Valve-regulated lead/acid (VRLA) batteries

In addition to the requirement for low-maintenance or maintenance-free lead/acid batteries, there is also a demand for sealed cells which may be used in any orientation. The problem lies in eliminating or accommodating the gas which is liberated on charging. Over the years many attempts have been made to develop sealed lead/acid batteries using the principle of catalytic H_2/O_2 converters sealed into the top of the cell. The catalyst was usually platinum or palladium deposited on a high-area support such as pelleted alumina. These devices were found never to be totally reliable, as they tend to flood with electrolyte in the pores, thereby isolating the catalyst and leading to the build-up of gas pressure.

The solution to the problem lay in *electrochemical* rather than catalytic recombination, with oxygen liberated at the positive electrode on charge being recombined electrochemically at the negative electrode. This process moves the potential of both electrodes in a positive direction and thereby inhibits hydrogen liberation at the negative. The problem then reduces to one of ensuring that the liberated oxygen has unfailing access to the negative electrode, not a simple matter in a flooded cell. This was solved by operating in a *starved electrolyte* mode whereby the acid is absorbed in the interstices of the separator, leaving sufficient voidage for the oxygen to pass through the separator to the negative plate. Two types of separator have been employed in VRLA batteries viz: absorptive glass-microfibre (AGM) separators and gel type separators. The latter are prepared by mixing very fine 'fumed' silica (particle size ~10 nm) with sulphuric acid and allowing to stand, when it undergoes gelation. When the gel has partially dried on standing, it develops cracks and fissures through which oxygen passes to
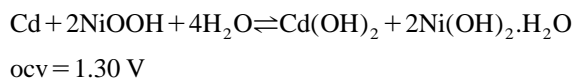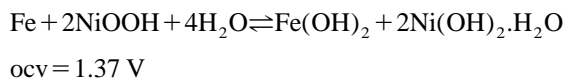
the negative electrode. Both types of separator have been employed successfully in sealed batteries. These batteries are always fitted with pressure release safety valves which accounts for their name (valve regulated lead/acid batteries). There is still considerable debate and discussion over the precise mechanisms by which these cells operate and also their modes of failure.

The first VRLA sealed cells were made in the 1970s as small (D size) cells by the Gates Corporation in the USA. The approach adopted was to take a single pair of positive and negative plates interleaved with an AGM separator and to spirally wind the assembly to form a cell (as in Fig. 3). VRLA batteries are now produced in a range of larger sizes in rectangular battery housings.

In summary, the advances which have been made in lead/acid battery technology over the past 50 years have been largely of a materials and design nature, involving the metallurgy of lead alloys, the manufacture of grids, the science of separators (both polymeric and glass-microfibre), the development of safety vents, high impact polypropylene battery housings and their sealing, and the internal cell-to-cell connectors.

5. Alkaline electrolyte secondary batteries

Rechargeable alkaline electrolyte batteries were invented at the end of the 19th century by Jungner in Sweden and Edison in the USA. These were based upon nickel oxide positive electrodes and either iron or cadmium negatives, and are popularly known as the 'nickel/iron' and 'nickel/cadmium' batteries, respectively. The electrolyte is concentrated KOH solution. The overall chemistry of each cell is analogous:

$$Fe + 2NiOOH + 4H_2O \rightleftharpoons Fe(OH)_2 + 2Ni(OH)_2.H_2O$$

ocv $= 1.37$ V

$$Cd + 2NiOOH + 4H_2O \rightleftharpoons Cd(OH)_2 + 2Ni(OH)_2.H_2O$$

ocv $= 1.30$ V

Both batteries were commercialised at an early date and have been subject to parallel research and

development over the years, especially as regards the common nickel oxide positive electrode.

5.1. Nickel oxide electrodes

There are four basic methods for preparing nickel oxide electrodes.

1. Pocket plate electrodes: this is the traditional method. The positive active material is contained in flat, rectangular channels (or 'pockets') made from perforated, nickel-plated steel strip (Fig. 5). The channels are then interlinked horizontally to form a plate. The active material consists of a mixture of $Ni(OH)_2$ and either nickel flake or graphite. The latter component is added to provide a conducting matrix. Often a few % of cobalt hydroxide is added to improve cell capacity and cycle life.
2. Plastic bonded electrodes: the electro-active materials are simply bonded into electrodes using a polymer binder. This is the lowest cost electrode, which finds widespread application in small rechargeable cells for consumer products.
3. Sintered plate electrodes: a porous nickel plaque is first prepared by lightly compacting nickel powder onto a perforated nickel screen or gauze and sintering in hydrogen at high temperature. The plaque should have ~80% porosity. It is charged with active material by chemical or electrochemical impregnation. These electrodes have a lower internal resistance than the above types and are capable of delivering higher specific energy and power.
4. Fibre electrodes: these latest electrodes are based upon compressed nickel fibres, or nickel felts or foams, which again are impregnated with the active material.

The latter two electrode types have been developed over the last 20–30 years and depend upon having appropriate starting materials, which are of fairly recent origin.
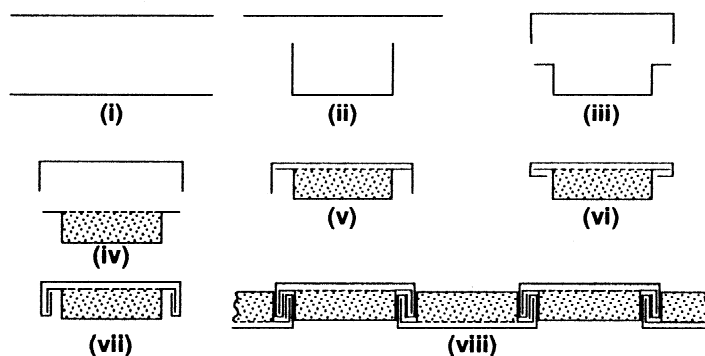
5.2. Nickel/iron batteries

Nickel/iron batteries found early industrial use as traction batteries in forklift trucks, mine and railway locomotives, etc. Usually, both the positive and

(a)
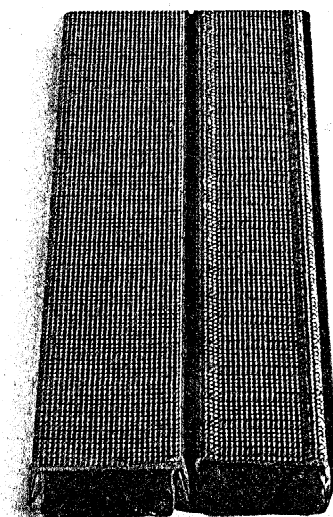
*The briquetting technique makes sure all active
material is compacted for good high rate performance.*

(b)

**Sequence of operations in fabrication of pocket plates for
nickel-cadmium batteries.**
(i) – (iii):   **Formation of channels in nickel-plated perforated steel strip**
(iv) – (vi):   **Filling and crimping to form a long continuous pocket**
(vii) – (viii): **Interlacing of filled strips and compression to form final plate**

Fig. 5. Construction of pocket plate nickel oxide electrodes.

negative electrodes were of the pocket plate type. The attraction of nickel/iron batteries is that they have 1.5–2 times the specific energy of lead/acid batteries and, relatively, are particularly good at high discharge rates (Table 2).

The battery is also noted for its ruggedness and long cycle life at deep discharge (2000 cycles at 80% DOD). However, compared to lead/acid it has several disadvantages:

Table 2
Comparative specific energies of Ni/Fe and Pb/acid batteries at two discharge rates

Rate (W/kg)	Ni/Fe (Wh/kg)	Pb/acid (Wh/kg)
20	54	36
40	50	26

- its low temperature performance is inferior;
- it has a comparatively high corrosion and self discharge rate;
- its overall electrical efficiency is poor because of a low over-potential for hydrogen evolution at the iron electrode. Considerable gassing on charge leads to a need for frequent maintenance.

For these reasons, the applications for Ni/Fe batteries have been limited in scope. Many attempts at solving the gassing problem have not been successful. The Ni/Cd battery has enjoyed greater success commercially as it is not subject to these limitations.

5.3. Nickel/cadmium batteries

After lead/acid, nickel/cadmium is the most widely used rechargeable battery. The cell operating voltage (1.20 V) is slightly less than that of Ni/Fe (1.25 V) and the mass of cadmium is higher than that of iron. Taken together, these two factors lead to a specific energy for the battery (30–40 Wh/kg) which is nearer to that of lead/acid than Ni/Fe. However, the high rate and low temperature performance is better than that of lead/acid. Other positive features of Ni/Cd batteries are a flat discharge voltage, long cycle life (~2000), continuous overcharge capability, low maintenance requirement and excellent reliability. Cells and batteries are available in many different sizes and with pocket-plate, plastic-bonded, or sintered electrodes. The principal disadvantages of Ni/Cd batteries are their high cost (up to 10 times that of lead/acid) and the environmental concerns associated with the disposal of batteries containing toxic cadmium.

Apart from the introduction of sintered electrodes, the improvements associated with Ni/Cd batteries over the past 50 years have been more in the area of cell design than in basic materials science. Traditional cells are of the vented variety and these are sold in large sizes for various applications. The reliability and low maintenance of the battery makes it ideal for stand-by power applications, whilst its high power output, maintained at low temperatures, makes it suited to the starting of large engines where 'cold-cranking' currents of 5000–10 000 amps may be required. Vented nickel/cadmium batteries also find

applications on railways, for marine duties, on board aircraft, and as traction batteries for mine locomotives, industrial trucks, etc.
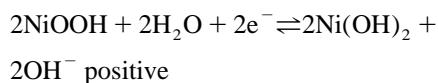
Over the past 40–50 years small, sealed Ni/Cd batteries have been introduced which can be used in any orientation. The capacity of these ranges from 10 mAh to 15 Ah. The KOH electrolyte is absorbed in several layers of reservoir separator, often a cellulosic material which allows free passage of oxygen liberated on charge to pass to the negative electrode where it is reduced. These sealed cells are analogous to the valve-regulated type of lead/acid battery as regards their recombination technology and also in having safety valves to relieve excess pressure. They are manufactured both as prismatic cells and as cylindrical cells, the latter as replacements for primary Zn/MnO_2 cells in standard sizes. Because of the lower voltage, a five cell Ni/Cd battery (6 V) replaces a four cell Zn/MnO_2 battery. The cylindrical cell may have either a spiral ('jelly-roll') construction, for high power output, or a bobbin construction, for higher volumetric capacity. Sealed Ni/Cd cells find their primary use in consumer applications, although special versions have been designed and used in telecommunications, and also in satellites and spacecraft. Nickel/hydrogen batteries are progressively replacing Ni/Cd for the latter application.

5.4. Nickel/hydrogen and nickel/metal hydride cells

There are relatively few negative electrode materials which can be used in strong alkaline solution, the most promising being cadmium, iron, zinc and hydrogen. The *nickel/hydrogen* battery has a sintered nickel oxide positive electrode and a platinum/hydrogen negative electrode. This battery was developed specifically to replace Ni/Cd in space applications on account of its higher specific energy content (ca. 50 Wh/kg) coupled to a very long life when subjected to deep discharge cycling.

The Pt/H_2 electrode is fully reversible and, when combined with a nickel oxide positive, forms a cell of potential 1.25 V. The cell reactions are as follows:

$$H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^- \quad \text{negative}$$

$$2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 +$$

$$2OH^- \text{ positive}$$

Note that there is a counterflow of water molecules and OH^- ions across the separator. The hydrogen gas liberated on charging is stored under pressure (~40 bar) within the cell itself. This necessitated considerable development work on the design and construction of the cell vessel, the cell stack and its supports, and the electrical leads through the cell wall. The pressure vessel is cylindrical in shape, with hemispherical end caps, and is constructed of thin gauge inconel alloy (Fig. 6). As the cell is cycled, the hydrogen pressure cycles also, from ~40 bar in the charged state to ~2 bar in the discharged state, and the pressure vessel must withstand this treatment without embrittling, corroding or cracking.

The cell stack is built up from back-to-back sintered nickel electrodes, electrochemically impregnated, and standard hydrogen fuel cell electrodes of platinum black dispersed on carbon paper. The separators are formed from a woven cloth of yttria-stabilised zirconia which absorbs the KOH elec-

trolyte. Ni/H_2 cells may be overcharged since liberated oxygen recombines at the negative electrode. Nickel/hydrogen space-cells are a sophisticated product which are exceedingly expensive to buy, but which nevertheless have largely usurped Ni/Cd for use in satellites.

Nickel/metal hydride cells are a later development of nickel/hydrogen for terrestrial applications. They depend on the principle that hydrogen may be stored reversibly in the form of a metal hydride which forms the negative electrode of the cell. The positive electrode is a standard nickel oxide electrode. Early work, in the 1970s, utilised $LaNi_5$ alloy as the negative; this takes up hydrogen reversibly at ambient temperature to form $LaNi_5H_{6.5}$. This alloy has a dissociation pressure of 1 bar at 15°C. Later commercial development work has focused on two new alloys to store hydrogen.

1. A complex alloy based upon the rare earth 'misch-metall' with various additives to adjust the dissociation pressure to the desired value and also to form a surface oxide film which acts as a barrier to prevent oxidation of the metal hydride.
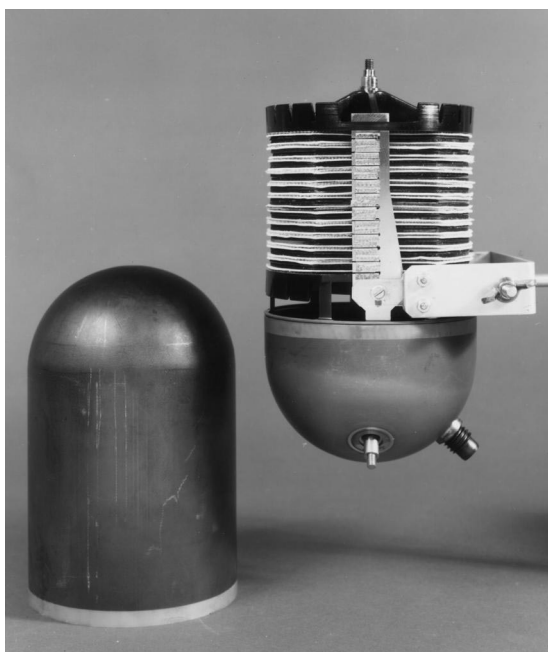

Fig. 6. 40 Ah nickel/hydrogen cell as used in satellites.

This is a proprietary formulation of the AB_5-type alloy, where A is a mixture of rare earths and B is partially substituted nickel.

2. A similarly complex, multi-component, alloy of the type AB_2, where A = Ti or Zr.

The latter is claimed to have higher hydrogen storage capacity, superior oxidation and corrosion resistance and to be less costly.

The operating voltage of a Ni/MH cell is almost the same as that of Ni/Cd (1.2–1.3 V), making for ready interchangeability, and the discharge curve is flat. The specific energy of Ni/MH batteries (60–70 Wh/kg) is 1.5–2 times higher than that of Ni/Cd and their specific power may be as high as 250 W/kg Batteries are resilient to overcharge and overdischarge and may be operated from −30 to +45°C. Cells of both cylindrical and prismatic design are now manufactured in a range of sizes; small cells are used in portable electronic devices (e.g. mobile phones), while prismatic cells of 100 Ah capacity are available for assembly into 12–14 V modules (e.g. for use as traction batteries). The new materials technology involved in the development of Ni/MH batteries is almost entirely associated with the hydride negative electrode.

6. Lithium ion batteries

Rechargeable lithium ion batteries represent an entirely new class of battery, developed and commercialised in the 1990s. They are now rapidly superseding alkaline batteries for a wide range of applications in the portable electronics field, and have potential for much larger cells and modules. The development of lithium ion batteries involves a challenging set of issues in materials science and technology, and research in this area is extremely active. Professor C.A. Vincent will be covering this topic in his lecture.

7. Future concepts

There are a number of other battery chemistries in an advanced stage of development, but not yet commercialised, for use in large-scale applications such as electric vehicle traction, storage in the electricity supply system, etc. The materials problems associated with these are outlined below.

7.1. Zinc/air batteries

Zinc/air primary batteries are well-known in small sizes for use in hearing aids and similar applications. However, all attempts to develop electrically rechargeable zinc/air cells have met with little success, primarily on account of the growth of zinc dendrites leading to internal short circuits. An alternative approach, now under serious development for large batteries, is to produce a *mechanically* rechargeable battery. This is essentially a large primary battery in which, at the end of discharge, the spent zinc hydroxide and KOH electrolyte are removed from the cell stack and returned to a central plant for recycling. There the slurry is electrolysed to produce fresh zinc powder which is returned to the battery stack. Such mechanical recharging is attractive because the positive reactant (atmospheric oxygen) is available in continuous supply and it is not necessary to develop a bifunctional oxygen electrode. Another advantage of mechanical recharging is that it may be accomplished in a few minutes, rather than the hours required for most electrical recharging.

The mechanically rechargeable zinc/air battery has been developed in Israel for use in electric vehicle traction. It has a high specific energy (200 Wh/kg), but only a modest specific power (100 W/kg at 80% discharge state). Modules comprise a stack of 66 cells and an eight module battery (150 kWh) has been built and tested in Germany in a Mercedes Benz 410 postal van. The vehicle had a range of 300 km between recharges.

In order to succeed with this mechanically rechargeable system, it was necessary first to develop three distinct units: the cell stack, the factory-based fuel regeneration plant, and the stack dismantling and refuelling machine. The first two posed both electrochemical and mechanical engineering problems, while the latter was a purely mechanical problem. The general approach adopted was to have a bed of zinc powder particles compacted on to a current collector frame and inserted in a separator envelope, flanked on both sides by air electrodes. This electrode assembly unit forms a cassette which

may be removed from the cell stack for recycling and replaced by a fresh cassette. The depleted cassettes are conveyed to a central facility for electrochemical regeneration to produce particulate zinc.

7.2. Zinc/bromine batteries

The zinc/bromine battery is an example of a 'flow battery' in which one of the reactants (bromine) is stored externally to the cell stack and flows through it during charge and discharge. The electrode reactions are

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \quad E^0 = -0.76 \text{ V}$$
$$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad E^0 = +1.065 \text{ V}$$
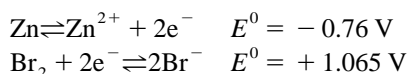
giving a cell voltage of 1.82 V. The electrolyte used is an acid (pH 3) solution of concentrated zinc bromide from which zinc can be plated. Several different manifestations of the zinc/bromine battery have been proposed, the most successful of which stores the excess bromine external to the cell as a complex with a quaternary ammonium bromide, such as an alkyl morpholinium bromide or alkyl pyrrolidium bromide. The complex of these salts with Br_2 is a dense, oily liquid which is immiscible

with water. When bromine is liberated during charge, the polybromide complex is formed as droplets, which separate from the aqueous electrolyte stream and are stored in a liquid reservoir external to the cell stack (Fig. 7). Zinc electroplates on the negative electrode in a satisfactory (non-dendritic) morphology, aided by the flowing electrolyte. On discharge, bromine is returned to the cell in the form of a dispersion of the polybromide oil in the aqueous electrolyte.

In principle, the construction of the cell stack and housing is straightforward, although there are materials problems stemming from the reactivity of bromine. A bipolar electrode is used, in which the conducting bipole plate is a lightweight carbon/plastic composite formed by extrusion. The separator, which is injection moulded, is housed in a non-conductive plastic frame which incorporates electrolyte flow channels. These stack components are lightweight and simple to manufacture, although the plastic employed has to be selected for stability towards bromine. Similarly the reservoirs, connecting tubing, pumps and gaskets all have to withstand degradation by bromine.

Considerable success has been achieved with this battery in several countries and a 22 kWh unit has been constructed and used to power an electric van.
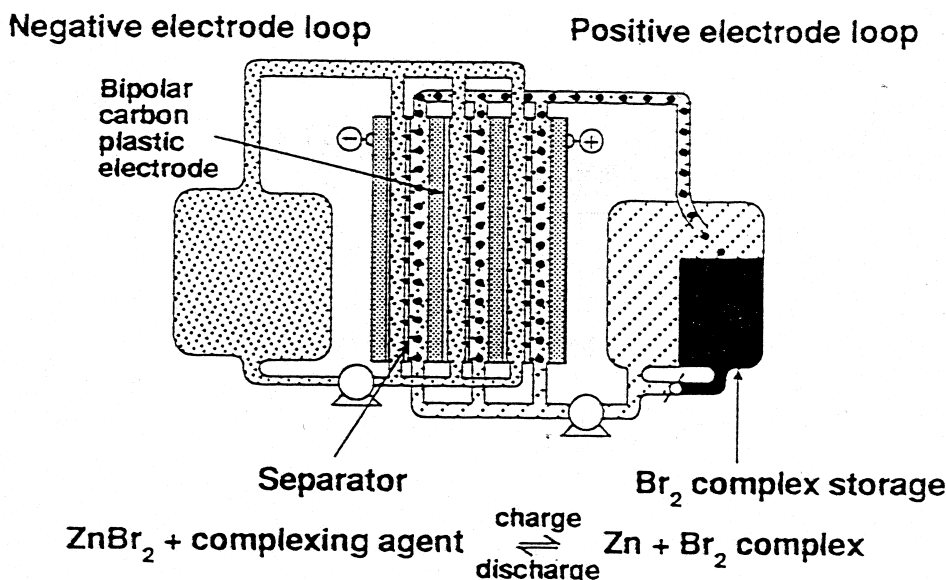

Fig. 7. Schematic of zinc/bromine battery.

This 108 V battery had a specific energy of 65–70 Wh/kg and a peak power density of 100 W/kg. An electric racing car has also been demonstrated powered by a Zn/Br_2 battery. Some concern has been expressed about the safety aspects of a battery incorporating bromine.

7.3. Redox batteries

There is growing interest in secondary redox batteries which possess a divided cell configuration, like the zinc/bromine battery, but which operate on the principle of the oxidation and reduction of ions in solution. The better known redox batteries involve the oxidation and reduction of cations in solutions separated by an anion exchange membrane which is nominally impermeable to cations. The cations in the two compartments may either be different (e.g. Cr^{2+} and Fe^{3+}) or the same, but in different valence states (e.g. V^{3+} and V^{5+}). As with the Zn/Br_2 battery, there are anode and cathode recirculating loops and the bulk of the reactant is stored outside of the cell stack in four external reservoirs, two for the reactants in the charged state and two in the discharged state. Pumps are used to circulate the reactant solutions. The capacity of the battery is limited only by the size of the storage tanks and, in this regard, the system is more akin to a fuel cell than a conventional battery. Although these batteries are bulky and have rather low specific energy and energy density, they hold the potential for low cost storage of electricity on a fairly large scale. The vanadium redox battery is being actively developed in Australia for the storage of solar electricity. The batteries are constructed on the 'plate and frame' principle using plastic components. As the reactant solutions are not chemically aggressive, unlike bromine, there are no serious materials problems to solve.

Recently a new type of Redox battery based on the oxidation and reduction of anions has been under development in the UK (the 'Regenesys'™ battery). This utilises a separator which is permeable to cations but not anions. During discharge the negative electrode reaction involves the oxidation of S^{2-} ions in Na_2S solution to sulphur, while the positive electrode reaction is the reduction of Br_2 dissolved in NaBr solution to Br^{2-} ions. The voltage of this cell is 1.57 V. The battery, which again is constructed on
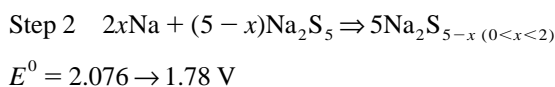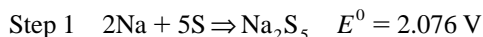
the plate and frame principle, is being developed on a large scale for load levelling in the electrical supply industry.

7.4. Sodium batteries

Sodium is most attractive as a negative electrode reactant on account of its high electrochemical reduction potential of -2.71 V (cf. Zn -0.76 V). When coupled with an appropriate electropositive material, it is capable of giving a cell of voltage >2 V. Moreover, sodium is abundant in nature, cheap and non-toxic. It is also of low atomic mass (23.0) and the combination of high voltage and low mass leads to the possibility of a battery of high specific energy. The disadvantages of sodium metal as a negative reactant is that an aqueous electrolyte cannot be employed and it is a potential fire hazard.

The realisation of a practical battery based upon sodium depended upon identifying a suitable non-aqueous electrolyte. This occurred in 1967 when scientists working at the Ford Motor Company in USA showed that sodium beta alumina, a form of sodium aluminium oxide, is highly conductive towards Na^+ ions at ~300°C, while being a good electronic insulator. This gave rise to the possibility of a solid ceramic electrolyte. They further demonstrated that, using this electrolyte in the form of a sintered ceramic tube, it is possible to construct a cell with a liquid sodium negative electrode and a liquid sulphur positive which operates effectively at 300–400°C. Since sulphur is an insulator, it has to be absorbed in a carbon felt electrode. The construction of the cell is shown schematically in Fig. 8. The practical construction is rather different as there are numerous materials science and engineering problems to be faced.

The cell discharges in two steps as Na^+ ions pass through the beta alumina to the sulphur electrode:

Step 1 $2Na + 5S \Rightarrow Na_2S_5$ $E^0 = 2.076$ V

Step 2 $2xNa + (5-x)Na_2S_5 \Rightarrow 5Na_2S_{5-x \, (0<x<2)}$

$E^0 = 2.076 \rightarrow 1.78$ V

In the first step, sodium polysulphide (Na_2S_5) is formed as a liquid, immiscible with liquid sulphur. The open circuit voltage is therefore invariant at
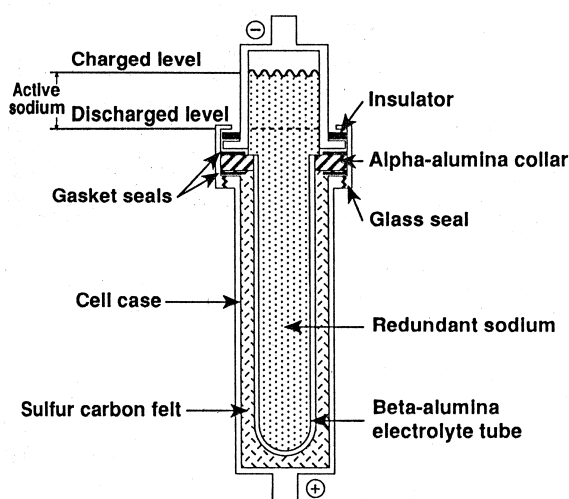
Fig. 8. Schematic of sodium/sulphur cell.

2.076 V. Once all the sulphur has been converted to Na_2S_5, an ionically conducting liquid, further discharge to Na_2S_3 takes place in a single phase and therefore the voltage declines linearly to 1.78 V at the composition Na_2S_3. These reactions are fully reversible on recharge.

The sodium aluminium oxide phase diagram is complex and a great deal of work has gone into optimising sodium beta alumina ceramic for this application. The specification for the electrolyte tubes (Table 3) is among the most stringent ever set for any ceramic material.

Many other problems were encountered in the

Table 3
Specification for beta alumina tubes[a]

High ionic conductivity at 300°C
Near theoretical density and impervious
High fracture toughness
Fine grain size and no flaws, for strength
Straightness and close dimensional tolerances
Good surface finish and closed end
Stable to moisture
Good wetting by sodium
Long life at high current densities
Resistant to electrical breakdown
High yield with reproducible properties
Rapid, low cost production

[a] After many years of research and development, this specification has largely been met by several manufacturers.

development of sodium/sulphur batteries. Among these were the following.

- Corrosion: hot sodium sulphide is highly corrosive to steels and other alloys. This poses a major problem for materials of cell construction.
- Seals: it is necessary to form an insulating seal between the two electrodes and also to seal each compartment against air ingress; chemical stability is a problem.
- Safety: unrestrained reaction between liquid sodium and liquid sulphur (in the event of electrolyte fracture) leads to a fierce fire and it is necessary to incorporate safety features in the cell design to prevent this happening.
- Top-of-charge problems: the Na/S cell has no overcharge mechanism and a fully charged cell is insulating. This means that in a chain of cells connected in series the first cell to reach top of charge experiences a high voltage across it which can lead to ceramic breakdown. This problem can only be avoided by connecting cells in a series/parallel array with many cross connections.
- Cell failure: a related problem is that when cells fail they tend to go open circuit, either immediately or after a while. Again, this calls for an automatic procedure to short circuit the failed cell or a small group of cells.

Although all of these problems have been addressed in detail, with some measure of success, most of the industrial development programmes have now been terminated (with the notable exception of that in Japan) for a mixture of technical and commercial reasons.

In parallel with the sodium/sulphur programme, there has been a development programme on a related battery system, the sodium/nickel chloride battery. This maintains many features of the Na/S battery (the beta alumina electrolyte, the sodium electrode, hot operation etc.) but replaces the liquid sulphur electrode by a solid nickel chloride electrode. The reversible cell reaction is:

$$Na + NiCl_2 \Rightarrow Ni + 2NaCl \qquad E^0 = 2.58 \text{ V}$$

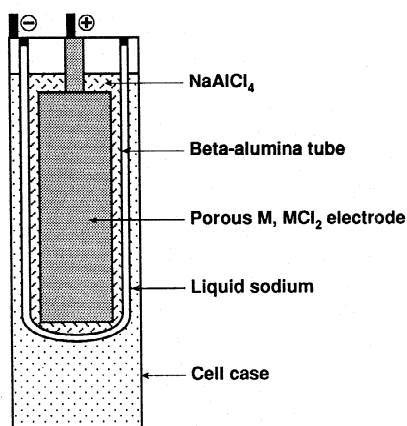A second (liquid) electrolyte, sodium chloraluminate $NaAlCl_4$, is added to the positive electrode

Fig. 9. Schematic of sodium/nickel chloride cell.

compartment so as to make good ionic contact between the solid $NiCl_2$ and the solid electrolyte (Fig. 9).

Experience with this cell showed that it has many advantages over the Na/S cell:

- it is assembled in the discharged state and charged only after sealing; this eliminates the need to handle liquid sodium;
- the raw materials employed are nickel powder and common salt, both commercially available and affordable;
- because the sodium is produced in-situ, by electrochemical reduction of Na^+ ions which have passed through the beta alumina tube, it is ultra-pure;
- the cell operates at a lower temperature (250–350°) than sodium/sulphur (300–400°);
- the cell has an overcharge and overdischarge mechanism which helps to balance out capacity inequalities between cells; series chains of cells are therefore possible with no cross-connections;
- a central positive cell design is employed and this eliminates corrosion problems; $NaAlCl_4$ is by no means as corrosive as sodium polysulphide;
- hermetic seals are easier to design and make for this battery;
- in contrast to Na/S, there are almost no safety problems with the $Na/NiCl_2$ battery;
- the nickel powder may readily be recovered from a discharged battery and recycled.

Although sodium batteries do not suffer from parasitic side reactions, as are commonly found in aqueous electrolyte batteries, their high temperature of operation inevitably results in some thermal loss which has to be made up electrically. This is effectively equivalent to a Faradaic inefficiency in a conventional battery. The development of vacuum enclosures however has reduced this loss to an acceptable level.

Development work on the sodium/nickel chloride battery for use in electric vehicles has been in progress for about 20 years in the UK, Germany and South Africa. A pilot production line has been built and full-size traction batteries manufactured for fleet trials in electric vehicles. The performance of these batteries has exceeded expectation in terms of reliability, ease of thermal control and lifespan. Electric cars and vans fitted with these batteries are an attractive proposition and the project has now been taken over by a company in Switzerland. Future development will require the construction of a full-scale manufacturing plant.

8. Conclusion

Over the past 50 years there has been a huge increase in market demand for batteries, principally as a result of the many new requirements for portable power in modern devices. Primary batteries are mostly confined to small sizes for use in the consumer market, although large primary batteries are needed in certain defence applications. Secondary batteries are used in both small and large applications.

The battery industry, ably supported by academic researchers, has responded to the challenge for improvements to existing batteries, as well as the development of entirely new battery types. Much of this development work has involved solving problems in materials science and fabrication technology. As a result we have greatly improved alkaline manganese cells, both primary and rechargeable, new types of maintenance-free lead/acid battery and sealed lead/acid battery, and better performance nickel/cadmium batteries. Among the new types of rechargeable battery which have become commercially available in the past decade, the nickel/metal

hydride and lithium ion cells are outstanding. Finally, a number of futuristic battery types are in an advanced stage of development particularly for large-scale applications such as electric vehicle traction, power storage in the electricity supply network and for use in conjunction with solar and other renewable energy resources. The future for enterprising companies in the battery industry looks promising.

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